Mercury Control with Calcium-Based Sorbents and Oxidizing Agents

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Abstract

Experiments were performed in a 1MW semi-industrial-scale, coal-fired facility, representative of a full-scale boiler. Southern Research Institute's spike and recovery system and procedures were used to obtain real-time gas-phase mercury-speciation measurements, with less than 5% uncertainty in the measured values. Previous quarter results indicated that ash composition was more important than chlorine content to Hg-speciation and capture, and the catalytic material in bituminous ash enhances Hg-oxidation and capture by calcium (i.e., PRB flyash and hydrated lime). It was shown that unburned carbon (UBC) is the dominant catalytic material of importance in flyash. Hence, other than UBC and to a lesser extent chlorine, other native flue-gas components are relatively unimportant to mercury oxidation and capture.

While it was previously shown that Hg-removal was most effective across the baghouse for dust cakes containing both high concentrations of calcium and UBC, it was not clear whether UBC enhanced Hg-capture only through enhancing Hg-oxidation or if the UBC also directly enhanced the reaction of oxidized mercury with calcium in the ash. It has now been shown that the presence of UBC in the baghouse filter cake is important for the capture of even oxidized mercury by high-calcium flyash or calcium-based sorbents. This is possibly due to reaction of sorbed HgCl₂ molecules (on UBC) with the calcium of adjacent particles. In any case, it is probable that carbon mixed with a calcium-based sorbent will enhance mercury capture, even if the mercury is already oxidized.

Sorbent development work in the recently constructed catalyst test facility at SRI is underway to find optimized compositions of calcium and carbon for mercury removal. Designer sorbents are sought that will allow the sorbent composition to meet the catalytic and sorbent needs of a particular coal type and power-plant efficiency. For example, a utility that produces a high-calcium, low-UBC flyash will need a different composition than a plant that produces a high-UBC, low-calcium flyash. Once an optimum calcium-based sorbent has been identified, it will be tested in the Combustion Research Facility at Southern Research Institute, for its effectiveness at mercury removal across an ESP and a Baghouse.

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Introduction

The predominant forms of mercury in coal-fired flue gas are elemental (Hg°) and oxidized (HgCl₂) [1-3]. The percentage of oxidized mercury in the stack effluent of a particular power plant depends on the coal type, combustion efficiency, and the pollution control equipment used. Essentially all of the mercury entering the furnace with the coal is vaporized and exists in the elemental form until the flue gases cool below ~600 °C (~1000 °F) [1-3]. The oxidation of mercury in coal-fired boiler systems is kinetically limited [1-3]. Because the concentration of mercury is very small in flue gas, any favorable mercury-oxidation reaction does not have the ability to promulgate itself. In virtually every conceivable competitive reaction, the competing gas component, much in excess of mercury, dominates. On the other hand, where the formation of mercuric compounds is thermodynamically favored, the kinetically controlled oxidation is generally slow unless the oxidant is in vast abundance compared with mercury.

In addition to the trace nature of mercury in coal-fired boilers, favorable reactions for mercury oxidation have short temperature/time windows. Consequently, the extent of mercury oxidation is highly dependent on catalytic processes. Heterogeneous catalysis enhances mercury oxidation reactions in two ways. First of all, disperse solid catalytic material provides sorption sites upon which reactions may take place. In addition, heterogeneous catalysis enhances mercury oxidation by effectively making available gas components (such as Cl⁻) that are otherwise scavenged by competing gas species present at much higher concentrations.

A system of reactions, which include significant chlorine-speciation reactions, has been proposed to describe homogeneous Hg-oxidation [4]. This set of governing reactions allows direct oxidation of Hg^o to HgCl and HgCl to HgCl₂ by the following four chlorine species with different reaction rates: Cl, Cl₂, HCl, and HOCl [4]. This system of equations has been shown to effectively predict mercury speciation for specific homogeneous systems [2]. However, the homogeneous model alone consistently under predicts the oxidation of mercury from coal-fired boilers [5]. Hence, it is important to identify and describe the heterogeneous reactions that dominate the mercury-oxidation process.

It has been shown in previous work [6,7] that UBC is the dominant catalyst naturally occurring in coal flyash, for Hg-oxidation enhancement. Niksa et. al. [8] suggested a possible mechanism whereby UBC can catalyze mercury oxidation, as follows:

$$UBC + HC1 \Leftrightarrow UBC.Cl + H \quad and \quad UBC.Cl + Hg^{0} \Leftrightarrow HgCl + UBC$$
 (1)

The March03 and June03 Quarterly Reports show that it is indeed the UBC that is responsible for the observed higher levels of oxidized mercury found in bituminous coal flue gas compared with PRB (high-calcium and low-UBC) flue gas [6,9,10]. There has also been evidence presented previously that calcium may be an effective sorbent for mercury, provided that sufficient UBC is present to help catalyze the capture. Although the data presented previously suggest that UBC is needed both to catalyze mercury oxidation and enhance mercury capture by calcium [6,7], it was not absolutely proven that the UBC was needed to enhance the capture of oxidized mercury by calcium. Hence, this quarter, the effectiveness of calcium sorbent at capturing oxidized mercury without UBC present was examined directly.

Experimental

The Combustion Research Facility (CRF) at Southern Research Institute (SRI) in Birmingham, AL, is a 1-MW_t semi-industrial-scale, coal-fired facility, which mimics the thermal profile of a full-scale boiler from the burner through the economizer. Figure 1 shows a two-dimensional sketch of this facility.

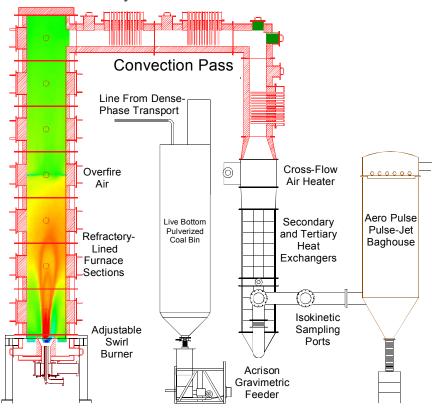


Figure 1. Combustion Research Facility (CRF).

Radiant Furnace

The furnace is a vertical, up-fired, 28-foot high cylinder, with an inner diameter of 3.5-feet (see Figure 1). This allows gas velocities of 10 to 20-feet per second and residence times of 1.3 to 2.5 seconds, depending upon the firing rate. The design furnace exit gas temperature is 2200 °F. As shown in Fig. 2, the temperature/time history of the CRF mimics that of full-scale power plants from the burner through the economizer.

Fuel Preparation

The fuel preparation area includes an open area storage yard, covered on-site storage bins, a rotary drum coal crusher, a CE Raymond bowl mill, and pulverized coal storage. The coal mill is a refurbished and instrumented Model 352 CE-Raymond bowl mill, which has a rated capacity of 2 tons per hour. This type of mill should give representative milling simulations of the different air-swept table and roller mills normally used in power plant service.

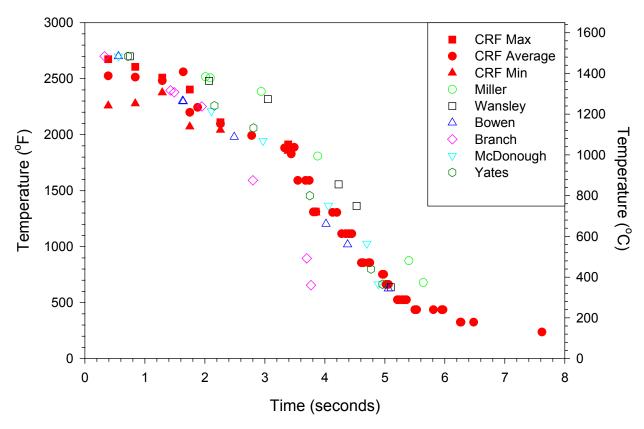


Figure 2. Combustion Research Facility (CRF) temperature/time histories compared with those of full-scale Southern Company coal-fired power plants.

Burner Assembly

The burner is mounted coaxially on the bottom of the furnace and is up-fired using natural gas, pulverized coal, any combination of the two or any other fuel that can be finely divided and transported to the pulverized coal silo. It is equipped with a flow control system for secondary air flow and a set of registers, which impart swirl to the secondary air, separate from the flow control. The secondary air and the primary air-coal mixture enter the furnace through a refractory quarl with a 25° half angle. Two clean-out ports are provided in this section, to allow bottom ash to be periodically removed from the furnace. A closed-circuit television camera with a control-room monitor allows constant monitoring of the view of the flame from the top of the furnace. A low NOx firing system, consisting of a generic dual-register burner and an overfire air system, can be installed to simulate several combinations of low NOx firing. The single-register burner was used for all experiments in the present investigation.

Convective Sections

The combustion gases exit the vertical furnace through a horizontal convection pass, which is designed to remove a substantial part of the heat from the flue gases. The extraction of heat was designed to simulate the time-temperature profile found in a utility boiler. A series of three air-cooled tube banks are installed in the convective pass, and the air cooling is used to control either the temperature profile of the flue gases or the tube metal surface temperatures for

fouling/ash deposition studies. A cross-flow tubular air preheater follows the convective tube banks and is used to preheat the primary and secondary air. Finally, four air-to-flue-gas recuperators are used to cool the flue gas down to a nominal 149 °C (300°F) before the flue gas enters the pollution control devices.

The convective section is 1.5 feet x 1.5 feet x 22 feet, providing gas velocities of 10 to 20 m/s (30 to 60 ft/s) and residence times of 0.4 to 0.8 seconds, again depending upon the firing rate. The design temperature range for the convective section is 1200 to 650°C (2200 to 1200°F).

Computer Data Acquisition and Control System

The facility is controlled and monitored by networked combined digital control system (DCS) and data acquisition computers, managed by Yokogawa CS-1000 system software that runs under the Windows NT operating system. This DCS performs all process control for the facility and allows complex feed-forward and calculated variable control. This computer control also performs the monitoring needed for safe operation of combustion equipment, including flame scanning and interlocks, automatic startup, and automatic shutdown of the entire facility. Process data acquisition and storage is accomplished within the Yokogawa software.

CEM System for Flue-Gas Composition

An extractive continuous-emissions monitoring (CEM) system measured the concentrations of CO, CO₂, NO_x, SO₂, and O₂ in the flue-gas exhaust. In addition, manual measurements of chlorine and moisture were obtained throughout the testing.

Pollution Control Equipment

Test equipment available for use at the Combustion Research Facility include an Electrically Stimulated Fabric Filter, a dry wall Electrostatic Precipitator, and a fluidized semi-dry / dry desulfurization system.

Permit Equipment

Particulate emissions are controlled by an Aeropulse pulse-jet baghouse, while sulfur dioxide emissions are controlled by an Indusco packed-column caustic scrubber. The pulse-jet baghouse and scrubber are required for the air quality permit of the facility issued by the Jefferson County Board of Health and are always on-line.

Combustor Operations

A routine facility operation is usually completed in one week, beginning at 8:00 am on Monday morning and ending at 5:00 PM on Friday afternoon. To facilitate start of testing on Monday morning the furnace is usually started on Sunday evening, firing with natural gas to heat up the system before switching to coal. It usually requires 12 hours before thermal equilibrium is achieved. The facility is operated 24 hours a day by two 12-hour shifts, during a test week.

Mercury Semi-Continuous Monitoring System

Mercury monitoring was performed with an advanced and customized semi-continuous Hg-speciation monitoring system. This Hg-SCEM has been customized to use an APOGEE Scientific QSIS probe for sampling flue gas. The QSIS probe is designed to pull a large volume of flue gas through an annulus within the probe at a high and turbulent velocity, thus scouring clean the walls of this annulus. The inner wall of the annulus contains a section with a porous frit through which a small sample of flue gas is drawn. The excess flue gas is directed back into the duct, downstream of the sample inlet. In this way, the QSIS probe allows a sample to be drawn from the duct without pulling it through an ash layer, thereby minimizing alteration of the gas sample – especially capture or oxidation of the vapor phase mercury by or on the particulate. Southern Research also developed a *continuous spike and recovery* system to validate the correctness of the mercury-speciation values measured. Because of these and other modifications, Southern Research Institute can now measure mercury speciation within a maximum uncertainty of 5%. Accurate and precise mercury speciation measurements are key to fundamental mercury speciation and capture investigations.

Spike and Recovery System

The *spike and recovery system* is a first of its kind prototype. The adaptation of this *spike and recovery* system to allow spiking at the tip of the APOGEE Scientific QSIS probe was performed by Southern Research personnel. The spike of mercury is introduced into the tip of the APOGEE Scientific QSIS probe far enough downstream from the inlet to prevent losses to the duct and far enough upstream of the porous annulus to allow complete mixing before the sampled gas is pulled through the porous frit. A relatively small quantity of air is used to carry the mercury spike to the probe. Therefore, dilution is insignificant, and the general flue-gas composition is undisturbed. The main impact of the spike is simply to increase the concentration of mercury in the sampled gas. This is significant, since mercury-oxidation processes that interfere with speciation measurements can involve three and four component interactions of flue-gas species on catalytic ash sites [11].

The concentration of mercury in the spike stream is generated by controlling the flow rate, pressures, and temperatures of air in and through a mercury reservoir. In addition, SRI uses a parallel Hg-source for the *spike and recovery* system, involving permeation tubes, allowing a check on the source calibration. High-precision mass-flow controllers are used to obtain the precise metering needed for high-certainty calibrated spikes. The proper use of *spike and recovery* provides a greater level of confidence in the resulting mercury speciation measurements than other methods currently in use. A schematic of the monitoring system is presented in Fig. 3, including spike location, gas-conditioning system, and calibrated spike source.

Figure 4 illustrates the use of the *spike and recovery system* for establishing total and oxidized mercury concentrations in the flue gas, while first burning natural gas (time 0:00 to 5:00) and then Black Thunder, a Powder River Basin (PRB) coal. As shown, the *spike recoveries* are observed on top of the measured initial mercury concentrations for both fuels.

The mercury speciation data were obtained well upstream of the baghouse. Table 1 contains the Hg-speciation measurements of the PRB flue gas, after validation using the *spike recoveries* shown in Table 2 (explained below).

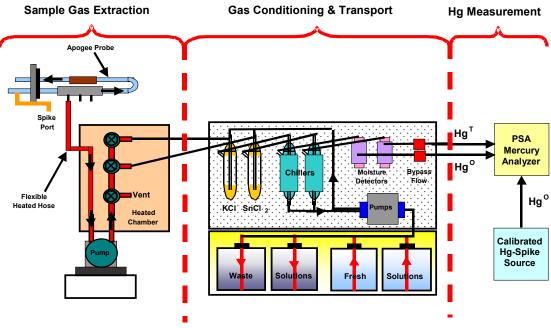


Figure 3. Mercury monitoring system, including spike and recovery.

Table 1. Location and speciation of Hg-measurements, while firing PRB coal (see Fig. 4).

Location	Temperature °C (°F)	Hg° $(\mu g/Nm^3)$	Hg^{T} $(\mu g/Nm^{3})$	Elemental Fraction %
After Recupatherm 1	260 (500)	7.4 +/- 0.93	8.4 +/- 1.1	88.1 +/- 1.5
After Recupatherm 2	163 (325)	6.5 +/- 0.44	8.0 +/- 0.70	81.3 +/- 1.0

• The mercury concentrations were measured with 6% oxygen in the flue gas.

The percentage of elemental mercury was measured directly (i.e., the population of individual measurements of Hg° and Hg^T, taken one after the other, were used to obtain the average and standard deviation for the elemental fraction), *not calculated* from the other values in the table.

Table 2. Spike recoveries while firing PRB coal.

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Sample	Temperature	Recovery 1	Recovery 2	Recovery 3	Ave Recovery
Type	°C (°F)	$(\mu g/Nm^3)$	$(\mu g/Nm^3)$	$(\mu g/Nm^3)$	/Spike (%)
Hg°	163 (325)	8.30	8.78	8.06	86.4
Hg^{T}	163 (325)	10.96	11.13	10.80	113.0
Hg°	260 (500)	7.91	8.24	7.81	82.4
Hg^{T}	260 (500)	11.59	11.64	11.06	117.8

• The Hg° spike injected into the tip of the sampling probe was ~9.7 μ g/Nm³.

As shown in Table 2, the recoveries of the elemental-mercury spike are consistently lower than the recoveries of total mercury. This is due to undesired oxidation in the Apogee

Probe and sampling lines. On the other hand, the stannous chloride (total Hg) impingers scavenge a significant quantity of CO₂, thus artificially raising the concentration of mercury in the sample gas. However, with *spike and recovery* these errors can be observed and eliminated. In this case (see Table 2), the spike recoveries were all within 20% of the expected value.

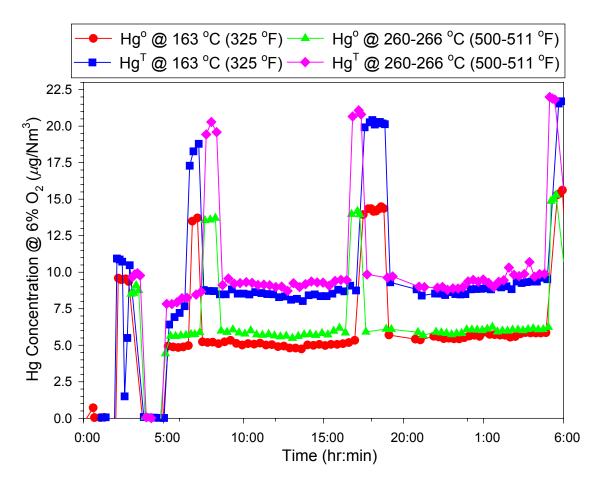


Figure 4. Mercury speciation data taken with an advanced and customized semi-continuous monitor and validated with *spike and recovery* for quality assurance.

As partially apparent in the data of Table 2, the difference in recoveries between expected and actual values was systematic, not random. In addition, as apparent in Fig. 4, there was little variation of the measured data for the flue-gas measurements or the spike-recoveries themselves. Using the *spike and recovery system* has allowed mercury speciation measurements with less than 5% uncertainty for all of the data presented in this report. This estimate of uncertainty is the standard deviation of corrected values added to the inherent uncertainty of the measurement technique.

Sampling Locations

For the mercury speciation investigation this quarter, measurements were made at the inlet and outlet of an Aero-Pulse pulse-jet baghouse, which uses full-scale Ryton-bags.

Coal Analysis

Tables 3 and 4 contain the analysis (including Hg and Cl) of the Choctaw America coal used in this work. As shown in Table 3, Choctaw America is a low chlorine coal. Other than chlorine content, Choctaw America is a typical eastern bituminous coal.

Table 3. Choctaw America HvA Bituminous coal analysis (from coal feeder discharge).

Proximate An	roximate Analysis (as rec.)		Ultimate analysis (daf)		Analysis (as rec.)
% Moisture	2.04	% Carbon	85.39		
% Ash	4.19	% Hydrogen	5.16	$Hg (\mu g/g)$	0.065 +/- 0.005
% Volatiles	31.76	% Nitrogen	2.04		
% Fixed C	62.01	% Sulfur	0.96	Cl (%)	0.0127
HV (Btu/lb)	14,019	% Oxygen	6.45		

Table 4. Mineral analysis of Choctaw America coal (from coal feeder discharge).

Species	Choctaw America
% Li ₂ O	0.06
% Na ₂ O	1.1
% K ₂ O	2.0
% MgO	1.1
% CaO	2.5
$\% \operatorname{Fe_2O_3}$	13.8
% Al ₂ O ₃	31.4
% SiO ₂	42.6
% TiO ₂	1.3
% P ₂ O ₅	0.16
% SO ₃	2.8

Results and Discussion

Previous work has shown that the presence of UBC in baghouse filter cakes enhances the capture of mercury by calcium, either from high-calcium flyash or from injected hydrated lime [6,7]. While the importance of having both UBC and calcium in the dust cake in order capture mercury by the calcium has been well established [6,7], the role of UBC in the mercury capture process is still debated. It is known that UBC is a very effective catalyst to enhance mercury oxidation (see Equ. 1). However, it was not clear whether or not calcium or hydrated lime alone would effectively capture mercury as long as the mercury was already oxidized.

In order to clearly identify the role of UBC in mercury capture by calcium (either in flyash or in sorbents) on baghouse filter cakes, two baghouses were used in series. Choctaw America coal was chosen because of its low-chlorine content and because its ash (generally producing about 4% UBC) is effective at enhancing the oxidation of mercury through baghouses. Therefore, in the test, the first baghouse was used to collect and remove the flyash from the flue gas stream and provide a filter cake that would enhance mercury oxidation. Hence, the flue gas leaving the first baghouse was free of particulate (including UBC) and yet contained very little chlorine and a mercury concentration that was highly oxidized. Some mercury was removed across the first baghouse, but because the Choctaw America coal ash is low in calcium, the removal was not more than 40%. The remaining mercury in the clean flue gas presented at the inlet to the second baghouse was over 80% oxidized. Figure 5 illustrates the configuration of the baghouses during the test.

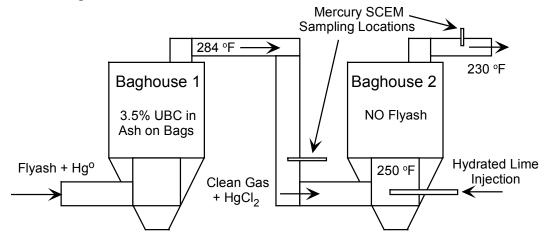


Figure 5. Duel baghouse test configuration.

As shown in Figs. 6 and 7, the inlet of the second baghouse contained 82% oxidized mercury and the outlet gas contained 83% oxidized mercury, while 28% of the total mercury entering the baghouse was removed in the baghouse. While the second baghouse was fairly clean, some residual ash remained on the bags from previous test runs, and this is why some mercury was removed across the baghouse. However, again shown in Fig. 7, when hydrated lime was injected into the second baghouse, mercury removal did not increase. Thus, it was not sufficient for UBC to catalytically enhance mercury oxidation prior to contact with calcium, in order to promote mercury capture by calcium. Even during hydrated lime injection, the mercury entering and leaving the baghouse was highly oxidized (>80%) (see Fig. 6).

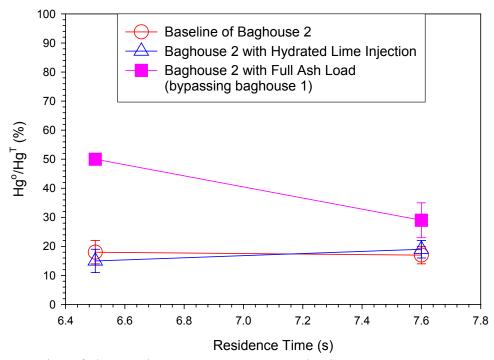


Figure 6. Fraction of elemental mercury present across baghouse 2.

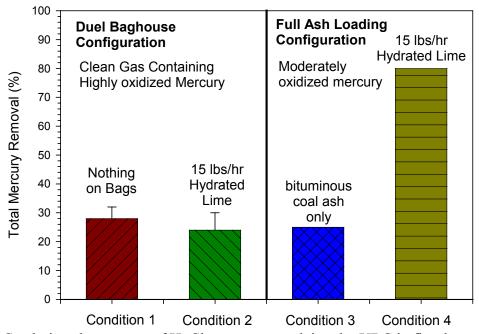


Figure 7. Catalytic enhancement of HgCl₂ capture on calcium by UBC in flyash.

As illustrated previously [12] and shown in Fig. 7, when the bituminous coal full-ash loading was allowed to enter the baghouse continually, the addition of calcium via hydrated lime injection was very effective at increasing mercury removal. For this case, shown in Fig. 7, hydrated lime injection increased the mercury removal from ~25% to ~80%. Hence, UBC plays a more extensive role in the enhancement of mercury capture by calcium than just to enhance

mercury oxidation. It is important for UBC to be present in the dust cake for effective mercury removal by calcium (high-calcium ash or calcium sorbents).

Baghouse 2 received somewhat lower-temperature flue gas than is typical for full-scale units. However, these lower temperatures were more favorable for UBC enhancement of Hg-capture by high-calcium ash or sorbent [7,9,13]. At much higher temperatures (i.e., air heater temperatures), reactions favorable to the direct capture of mercury by calcium may occur, without the presence of UBC.

One possible mechanism whereby UBC may enhance mercury capture by calcium is by providing a sorption site for mercury to attach through van der Waals' forces, thus slowing the mercury molecules down and bringing them in contact or near contact with adjacent calcium sites where reactions may take place. In fact, the reaction of elemental mercury with chlorinated carbon sites, i.e., UBC.Cl- (see Equ. 1), followed by reaction with nearby calcium sites, may provide a semi-direct pathway for the capture of elemental mercury by calcium in baghouse filter cakes.

It is true that most (not all) of the UBC present in bituminous coal ash is in separate particles from the rest of the flyash [14], and in a filter cake, the carbon is not intimately associated with the calcium injected as a sorbent. Nevertheless, there may be a sufficient number of contact sites between carbon and calcium, to allow a significant mercury capture enhancement to occur. Furthermore, PRB coal ash typically retains its relatively small percentage of UBC on the surface of high-calcium ash particles, thus making the prospects of a two-step (oxidation/capture in the case of Hg° and sorption/capture in the case of HgCl₂) reaction even more likely.

Sorbent development is being pursued based on this understanding of general global mechanisms in real coal-fired flue gas and under conditions, including temperature/time histories, that are relevant to full-scale boiler systems. The recently constructed catalyst test facility (CTF) at Southern Research Institute has been adapted this quarter for mercury sorbent development. The CTF will be used in the next quarter to optimize sorbent compositions for most effective mercury removal. Optimized sorbents will be tested in the CRF for most effective mercury removal in a baghouse and/or ESP. Eventually, designer sorbents are sought that will have compositions specifically designed for each individual power station coal type, system, pollution control devices, and operating conditions.

Figures 8 and 9 show pictures of the CTF's quartz furnace, gas-conditioning bubblers for mercury speciation and stabilization prior to mercury monitoring, flue-gas continuous emission monitors (CEMs), and gas-flow control systems. Both elemental and total mercury will be measured at the outlet of the CTF. The CTF will simulate clean flue gas with all the major flue-gas species present, including CO, CO₂, H₂O, O₂, N₂, HCl, NO, SO₂, SO₃, and Hg°, in concentrations that exist in the flue gases of existing power plants, burning specific coal types. The sorbent bed and furnace temperature will be varied as needed to assess different sorbent utilization conditions and strategies. Even the most rigorous of bench-scale experiments are not sufficient to mimic the full-scale conditions of a coal-fired power plant. Therefore, the CTF will only be used for comparison with known effective mercury sorbents and for optimization prior to testing in the pilot-scale unit, where conditions are comparable to full-scale units.

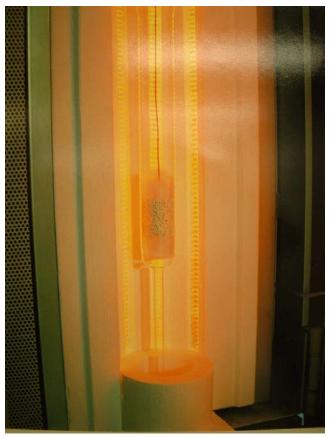


Figure 8. CTF quartz furnace with catalyst at ~1000 °C.



Figure 9. CTF furnace, gas-injection system, flue-gas CEMs, and Hg gas-conditioning system.

Conclusions

Research conducted on this project in *previous* quarters [6, 9] has produced the following conclusions:

- 1) Unburned carbon (UBC) in ash is the overwhelming primary component responsible for the difference observed in vapor-phase mercury speciation between Powder River Basin (PRB) sub-bituminous coal flue gas and bituminous coal flue gas.
- 2) Increased UBC in ash is the primary component responsible for coal-blending enhancement of mercury capture on high-calcium (PRB) ash.
- 3) Unburned carbon enhances mercury capture on calcium by catalytically enhancing mercury oxidation prior to capture.

Furthermore, from the *previous* work on this project [6, 9], it has been postulated that UBC may enhance Hg-capture by catalytically enhancing the capture of oxidized mercury by calcium.

The results *this quarter*, from the dual-baghouse test, have provided more evidence to support this postulate. Although the carbon and calcium in flyash are not intimately associated for all flyash types, some contact between the carbon in ash and the calcium does occur, which may provide some opportunity for sorption followed by capture.

It has been shown in this report and previously that hydrated lime is effective at capturing mercury in a baghouse, even for low-chlorine flue gas, when a bituminous coal is fired that produces a moderate UBC concentration (i.e., 3.5%) in the ash.

The results of this investigation show that it is not sufficient to oxidize the mercury in order for it to be captured by calcium. Unburned carbon is needed in the dust cake in order for hydrated lime or high-calcium ash to be effective at removing mercury, at typical baghouse temperatures (i.e., 230 °F to 300 °F). This enhancement of mercury removal on calcium by the presence of UBC is possibly due to sorption of oxidized mercury onto UBC sites followed by reaction with adjacent calcium sites. Chlorinated UBC sites may also provide a semi-direct pathway for the capture of elemental mercury by first reacting with elemental mercury to form HgCl₂ followed by immediate capture by an adjacent calcium site.

Future Work

The present and previous results from this project thus far yield information from which the following future tests were conceived.

- 1) Sorbent development investigations are already underway to utilize the information obtained on UBC catalysis and mercury speciation. The composition of these designer sorbents will be optimized using the modified Catalyst Test Facility (CTF) at SRI. An optimized sorbent will be tested in the CRF to observe the ability of this designer sorbent to remove mercury in the disperse phase, through an ESP, and in a baghouse.
- 2) Sodium tetrasulfide injection will be tested in the CRF for its ability to remove mercury across an ESP

3) Finally, field-testing options will be explored for promising technologies. One such option is Na₂S₄-injection in the slipstream ESFF baghouse at Plant Miller, scheduled for this December. Should the test be successful, additional funding will be sought for full-scale demonstrations. This test at Plant Miller will be paid for by EPRI.

References

- 1. Gale, T. K., "Mercury Control with Calcium-Based Sorbents and Oxidizing Agents" Quarterly Report DE-PS26-02NT41183 for period Oct. 1st through Dec. 31st, 2002.
- 2. Senior, C. L., Chen, Z., and Sarofim, A. F., "Mercury Oxidation in Coal-Fired Utility Boilers: Validation of Gas-Phase Kinetic Models", *A&WMA 95th Annual. Conference.*, Baltimore MD, (2002).
- 3. Niksa, S., Helble, J. J., Fujiwara, N., "Kinetic Modeling of Homogeneous Mercury Oxidation: the importance of NO and H₂O in predicting oxidation in coal-derived systems", *Environ. Sci. Technol.*, **35**: 3701-3706 (2001).
- 4. Niksa, S., Fujiwara, N., Fujita, Y., Tomura, K., Moritomi, H., Tuji, T., and Takasu, S., "A Mechanism for Mercury Oxidation in Coal-Derived Exhausts" *J. A&WMA* **52**: 894-901 (2001).
- 5. Chen, Z., Senior, C. L., and Sarofim, A. F., "Modeling of Mercury States in Coal-Fired Utility Boilers" *27th Annual Technical Conference on Coal Utilization and Fuel Systems*, Clearwater Florida, March 4-7 (2002).
- 6. Gale, T. K., "Mercury Control with Calcium-Based Sorbents and Oxidizing Agents" Quarterly Report DE-PS26-02NT41183 for period Apr. 1st through Jun. 30th, 2003.
- 7. Gale, T. K. and Merritt, R. L., "Coal Blending, Ash Separation, Ash Re-Injection, Ash Conditioning, and Other Novel Approaches to Enhance Hg Uptake by Ash in Coal-Fired Electric Power Stations" *International Conference on Air Quality IV, Mercury, Trace Elements, and Particulate Matter*, Arlington, VA, September 22-24, 2003.
- 8. Niksa, S. and Fujiwara, N., "Predicting Mercury Speciation in Coal-Derived Flue Gases", EPRI-DOE-EPA-A&WMA Combined Utility Air Pollution Control Symposium: The MEGA Symposium, May (2003).
- 9. Gale, T. K., "Mercury Control with Calcium-Based Sorbents and Oxidizing Agents" Quarterly Report – DE-PS26-02NT41183 for period Jan. 1st through Mar. 31st, 2003.
- 10. Gale, T. K., "Mercury Control with Calcium-Based Sorbents and Oxidizing Agents" DOE Mercury Control Technology R&D Program Review Meeting, Aug. 12-13, 2003.

- 11. Norton, G. A., "Effects of Fly Ash on Mercury Oxidation During Post Combustion Conditions", Annual Report DE-FG26-98FT40111 for period Sept 1st, 1999 through Aug. 31st, 2000.
- 12. Gale, T. K., "Mercury Control with Calcium-Based Sorbents and Oxidizing Agents" Topical Report-DE-FC26-01NT41183 for period Sept. 5th 2001 through May 31st 2002.
- 13. Gale, T. K., Merritt, R. L., Cushing, K. M., and Offen, G. R., "Mercury Speciation as a Function of Flue Gas Chlorine Content and Composition in a 1 MW Semi-Industrial Scale Coal-Fired Facility", *EPRI-DOE-EPA-A&WMA Combined Utility Air Pollution Control Symposium: The MEGA Symposium*, May (2003).
- 14. Hurt, R. H. and Gibbins, J. R., "Residual Carbon from Pulverized Coal Fired Boilers: 1. Size Distribution and Combustion Reactivity", *Fuel* **74**(4): 471-480 (1995).